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Effect of ammonium carbonate on formation of calcium-deficient hydroxyapatite through double-step hydrothermal processing

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Abstract Double-step hydrothermal processing is a process where powder compacts of calcium phosphates are exposed to vapor of solvent solution, followed by being immersed in the solution. In the present study, we investigated the effects of ammonium carbonate on formation of calcium-deficient hydroxyapatite (CDHA) through double-step hydrothermal processing. The synthesized CDHA has high crystallinity when the solution has relatively low concentration of the ammonium carbonate ranging from 0.01 to 0.25 mol dm^{-3}. Carbonate content in the prepared samples were distinctly increased with increasing the concentration of ammonium carbonate to indicate formation of carbonate-containing calcium-deficient hydroxyapatite (CHAp) with low crystallinity. Morphology of the CHAp formed on the compacts varied progressively from rods and rosette-like shape to irregular shape with increase in the initial concentration of the ammonium carbonate in the solution. Application of ammonium carbonate in the double-step hydrothermal processing allows fabrication of irregular-shaped CDHA containing carbonate ions in both phosphate and hydroxide site, with low crystallinity, when the initial concentration of ammonium carbonate was 0.5 mol dm^{-3} and more.

1 Introduction

Hydroxyapatite (HAp) is a type of bioactive ceramics that shows osteoconductivity when implanted in bone defects. Stoichiometric composition of HAp is generally given as $Ca_{10}(PO_4)_6(OH)_2$. The biological activity and degradability are affected by the compositions of HAp since the solubility of HAp varies with its compositions such as substitution of sodium (Na^+), magnesium (Mg^{2+}) and carbonate (CO_3^{2-}) ions in the compositions. HAp naturally allows non-stoichiometric compositions such as calcium-deficient hydroxyapatite (CDHA). Hence, carbonate-containing CDHA, i.e. carbonated hydroxyapatite (CHAp), is an important candidate as a biomaterial for bone reconstruction, due to the similarity of the compositions to natural bone. Namely, CHAp is expected to show high potential of osteoconduction as well as biodegradability. Thus fabrication of CHAp is one of the attractive researches for development of bone substitutes. In the HAp structure, carbonate ion can substitute hydroxide ion (OH^-), phosphate (PO_4^{3-}) ion or both and is called as A-type, B-type and AB-type substitution, respectively [1, 2]. On preparation of CHAp, several processings utilizing wet conditions such as gel [3], sol–gel [4], electro-chemical deposition [5], precipitation [6] and hydrothermal processing have been used. Among these processings, hydrothermal method has advantages such as cost effectiveness, easy control of nucleation, high dispersion, high reaction rate, shape control, phase purity and homogeneity [7].

Calcium phosphate blocks, are widely used in clinical applications since they show high biological affinity implying osteoconductivity and biodegradability. They are used to fill bony defects following dental or cranio-facial surgery [8]. Designed macrostructure has been receiving attention to improve not only biological properties but also mechanical properties like bending strength, tensile strength and fracture toughness. Therefore bone replacement materials of desired shape are a necessity for specialized applications. Hence it is advantageous to prepare

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CHAp as blocks for the above biological applications. However, it is still difficult to synthesize a block of CHAp that is available as bone substitute on dental and orthopedic application. Although Ishikawa et al. reported synthesis of needle-like CHAp through a dissolution-precipitation process starting from calcium hydroxide via a formation of gypsum with calcite [9], they provided little information on control of morphology and compositions of the fabricated CHAp blocks. To fabricate HAp block, Watanabe et al. [10] recently reported double-step hydrothermal processing of a mixture consisting of two types of calcium phosphates, namely beta-tricalcium phosphate (*β*-TCP, $Ca_3(PO_4)_2$) and dicalcium phosphate dihydrate (DCPD; $CaHPO_4{\cdot}2H_2O$). The double-step hydrothermal processing consists of treatment of calcium phosphates by exposure to vapor of a solution, followed by immersion in the solution. This processing is expected to allow formation of a HAp block with unique morphology controlled through selected reactants of not only *β*-TCP, DCPD but also HAp, alpha-tricalcium phosphate (α-TCP, $Ca_3(PO_4)_2$) and dicalcium phosphate anhydrous (DCPA, $CaHPO_4$). The selectivity of the reactants allows controlling the composition of the HAp products, since HAp has a compositional variation to form non-stoichiometric compounds.

In this study, we examined feasibility of fabrication of CHAp block through the double-step hydrothermal processing from a mixed powder consisting of *β*-TCP and DCPD by a treatment with aqueous solution containing ammonium carbonate. Morphology, carbonate contents and crystalline phases of the calcium phosphate specimens were characterized to understand the effects of carbonate addition from ammonium carbonate by double-step hydrothermal processing for preparation of a CHAp block.

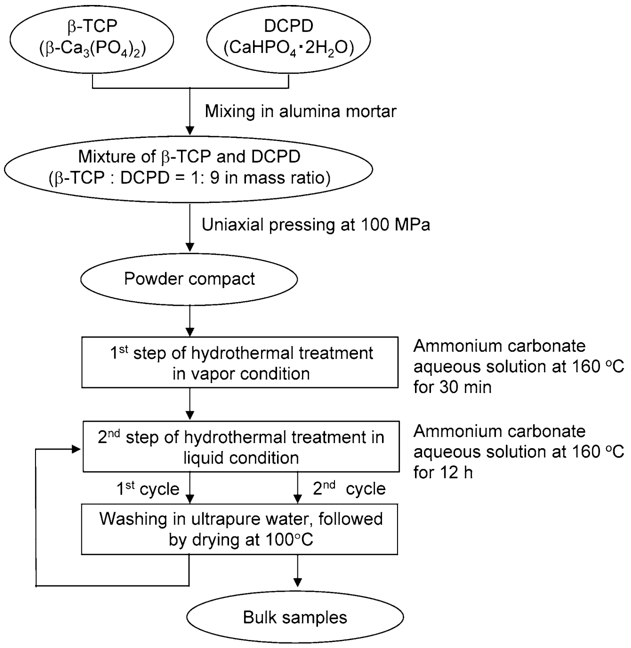
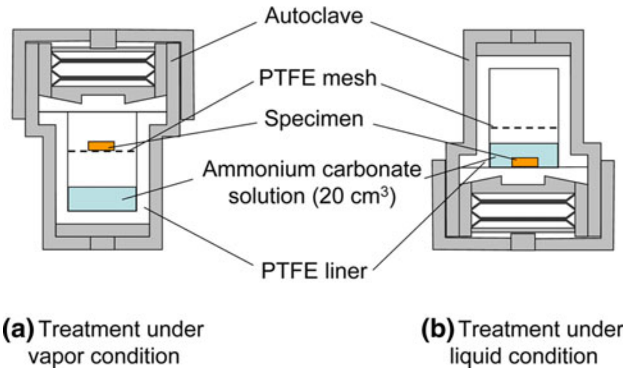


Fig. 1 Workflow of the preparation of the samples by double-step hydrothermal processing in this study



(a) Treatment under vapor condition

(b) Treatment under liquid condition

Fig. 2 Schematic setup for hydrothermal processing under **(a)** vapor and **(b)** liquid conditions

2 Experimental procedure

2.1 Double-step hydrothermal treatment

The present study adopted modified procedure of the double-step hydrothermal processing reported by Watanabe et al. [10]. The experimental workflow is shown on Fig. 1. A powder mixture of *β*-TCP (Taihei Chemical Industrial Co., Ltd., Osaka, Japan) and DCPD (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was prepared at a mass ratio of *β*-TCP:DCPD = 1:9. 0.2 g of the mixed powder was then subjected to uniaxial pressing at a pressure of 100 MPa to make a compact of 1 cm in diameter and 0.15 cm in height. The powder compact was placed in a vessel of 9 × 10 cm^3 with 20 cm^3 of an aqueous solution containing various concentrations of ammonium carbonate. The ammonium carbonate (Kishida Chemical Co., Ltd., Osaka, Japan) was used as-received, provided its estimated formula was $(NH_4)_2CO_3$, to be dissolved at a concentration ranging from 0.01 to 1 M (= mol dm^{-3}). The apparatus for the double-step hydrothermal processing is shown on Fig. 2. The vessel was sealed and placed in an oven at 160°C. After the initial interval of 0.5 h for rising the temperature, it was kept for 0.5 h with the vapor exposure. Then the powder compact was soaked within the solution by turning over the vessel and kept for 12 h (first cycle). After renewal of the solution, the compact was immersed in the solution for 12 h (second cycle). The hydrothermally treated samples were thoroughly washed with deionized water and dried. Let the samples treated with 0.01 M, 0.25 M, 0.5 M, 0.75 M, 1.0 M of ammonium carbonate be denoted as 0.01MCHAp, 0.25MCHAp, 0.5MCHAp, 0.75MCHAp, 1.0MCHAp, respectively. The calcium phosphate compact was also treated in NH_4Cl/NH_3 buffer solution with an NH_4Cl concentration of 2 mol dm^{-3} adjusted to pH = 9.12 and was used as control sample, since the pH of the ammonium carbonate solution was around pH = 9.

2.2 Characterization

Ca/P atomic ratio of the prepared samples were determined using inductively coupled plasma—atomic emission spectroscopy (ICP-AES; Optima 2000DV, PerkinElmer Japan Co., Ltd., Yokohama, Japan), after the samples were dissolved in 5 vol% nitric acid solution. Fourier transform infrared (FT-IR) spectroscopy was conducted with JASCO FT-IR-610 spectrometer (JASCO Co., Tokyo, Japan) using KBr pellet technique. Thermogravimetric analysis (TGA; Thermoflex TAS 300 TG8101D, Rigaku Co., Tokyo, Japan) was conducted up to 1,000°C for determining carbonate content in the synthesized samples. The carbonate content was estimated by weight loss of the samples from 500 to 1,000°C. Powder X-ray diffraction (XRD) patterns was recorded using RINT PC2100 (Rigaku Co., Japan) diffractometer with CuKα radiation. The lattice parameters were determined using CELREF unit cell refinement software program [11]. The surface morphology of the prepared blocks were observed using scanning electron microscope (SEM; JSM-5600, JEOL Ltd., Tokyo, Japan), following coating of the samples with gold film by a sputtering coater (JEOL JFC-1300, JEOL Ltd.).

3 Results

3.1 Compositions

Table 1 gives Ca/P atomic ratios of the prepared samples determined by ICP-AES analysis. The pH of the solutions before and after the hydrothermal treatment is also given along with the morphology on the surface of the prepared blocks observed under SEM, which is described in Sect. 3.3. The control sample shows Ca/P atomic ratio less than 1.67 that is stoichiometric atomic ratio of HAp. The Ca/P atomic ratio of the samples increased with increasing initial concentration of ammonium carbonate in the range from 0.01 to 0.50 M. For sample 1.0MCHAp, the Ca/P atomic ratio was comparable to control sample (1.60). Increase in Ca/P atomic ratio means substitution of phosphate ion by carbonate ion that is referred as B-type substitution, while substitution of hydroxide site with phosphate ion (A-type substitution) does not change the Ca/P atomic ratio. The substitution site of the carbonate ion was investigated by FT-IR spectroscopy (Fig. 3), where the assignment of the A-type and B-type substitution according to previous reports are given [12]. The characteristic bands for PO_4^{3-} groups at 565, 604, 1,000–1,100 cm^{-1} and a band corresponding to OH^- group at 634 cm^{-1} were also observed on the spectra. Bands owing to carbonate (CO_3^{2-}) groups appeared at 878, 1,547 cm^{-1} (A-type substitution) and 1,412, 1,458 cm^{-1} (B-type substitution). Also, the band of OH^- group at 634 cm^{-1} progressively decreased with

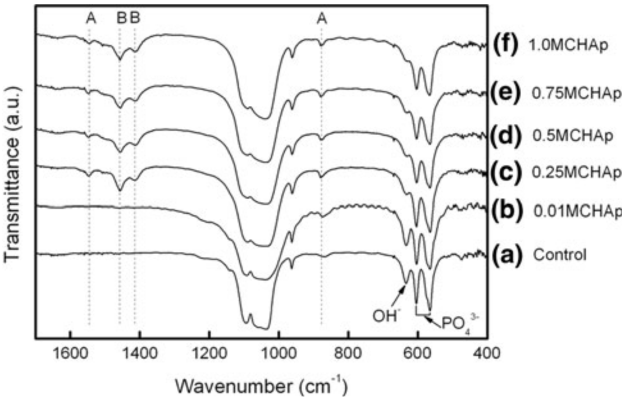


Fig. 3 FT-IR spectra of (*a*) control and the samples prepared by the double-step hydrothermal processing using an ammonium carbonate solution at initial concentration of (*b*) 0.01 M, (*c*) 0.25 M, (*d*) 0.5 M, (*e*) 0.75 M and (*f*) 1.0 M. *Broken lines* with A and B are assigned to A-type and B-type substitution, respectively

Table 1 Characteristics of the synthesized samples

Sample	Ca/P atomic ratio	Morphology	Length (μm)	pH of the initial solution	pH of the final solution
Control	1.60	Rod	1–2	9.12	9.2
0.01MCHAp	1.61	Rod	10–15	9.33	7.78
0.25MCHAp	1.64	Rosette-like	1	8.92	9.37
0.5MCHAp	1.66	Featureless	n.d.	8.93	9.13
0.75MCHAp	1.66	Featureless	n.d.	8.85	9.25
1.0MCHAp	1.60	Featureless	n.d.	8.87	9.21

n.d. not determined

increasing concentration. This is attributed to substitution of OH^- group by the CO_3^{2-} groups along the crystallographic *c*-axis [13]. Both A-type and B-type substitutions were detected on the spectra of the samples prepared through the double-step hydrothermal processing of the calcium phosphates with ammonium carbonate solution. Higher concentration of the ammonium carbonate in the initial solution gave more distinct absorption spectra assigned to AB-type substitution. The degree of the AB-type substitution increased with increasing initial concentration of the ammonium carbonate. TGA was employed to determine the carbonate contents of the synthesized samples. A typical TGA pattern used to determine carbonate content of control and 0.75MCHAp samples are shown on Fig. 4. The weight loss up to 500°C is due to removal of water (adsorbed and lattice) and acidic phosphate if present. The acidic phosphate is converted to phosphate by the following reaction:

$$2HPO_4^{2-} + CO_3^{2-} \rightarrow PO_4^{3-} + H_2O + CO_2$$

The weight loss occurring from 500 to 1,000°C is due to decomposition of carbonate ions [14, 15]. The hydroxyl weight loss occurs after 1,000°C leading to formation of oxyapatite. Figure 5 shows summary of the relationship between the measured carbonate contents and Ca/P atomic ratios of the prepared specimens in the present study. The compositional analysis of the samples showed that Ca/P atomic ratios increased with increasing contents of carbonate in the samples up to approximately 1.5 mass%, when the initial concentration was 0.5 M. When the initial concentration of the ammonium carbonate was 1.0 M, the Ca/P atomic ratio of resultant sample decreased to 1.60, which is comparable to that of control sample.

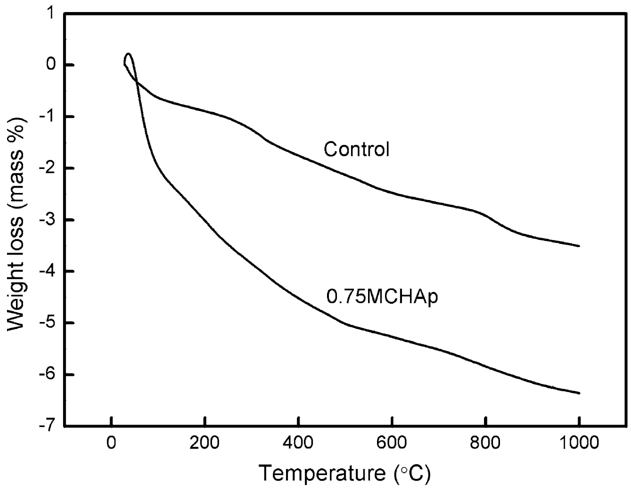


Fig. 4 TGA of control and sample prepared by the double-step hydrothermal processing using an ammonium carbonate solution at initial concentration of 0.75 M. The carbonate weight loss was calculated from 500 to 1,000°C

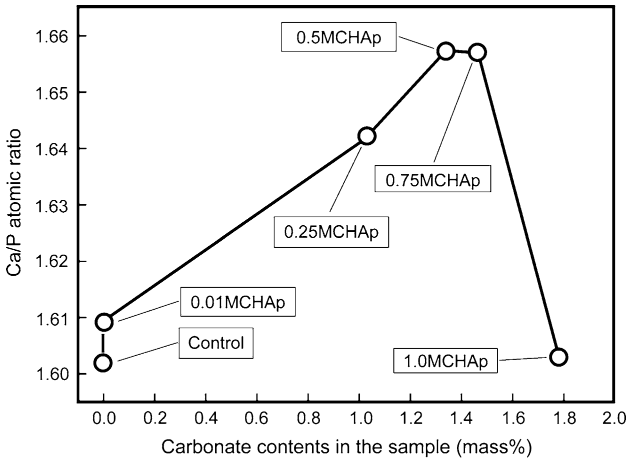


Fig. 5 Relationship between Ca/P atomic ratios as a function of carbonate contents determined by thermogravimetric analysis

3.2 Crystalline phase

Figure 6 shows the powder X-ray diffraction patterns of the prepared samples. The X-ray diffraction patterns confirmed that all the peaks are assigned to HAp according to PDF #76-0694, with no extra phase. Samples control, 0.01MCHAp, 0.25MCHAp showed sharper peaks, which implied that the samples formed had higher crystallinity than samples 0.5MCHAp, 0.75MCHAp and 1.0MCHAp. The crystallinity decreased for samples 0.5MCHAp, 0.75MCHAp and 1.0MCHAp as their peaks on the diffraction patterns were comparatively broad. Figure 7 shows the lattice parameters of the samples, provided the formed CDHA would be a hexagonal system. The variation of lattice parameters "*a*" and "*c*" obtained from the X-ray diffraction patterns were plotted with respect to carbonate contents of the samples. Both the axes slightly decreased with increasing carbonate contents of the blocks. Such a

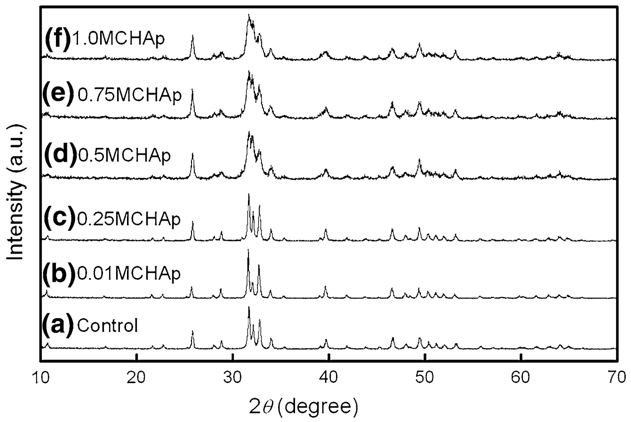


Fig. 6 Powder X-ray diffraction patterns of (*a*) control and the samples prepared by the double-step hydrothermal processing using an ammonium carbonate solution at initial concentration of (*b*) 0.01 M, (*c*) 0.25 M, (*d*) 0.5 M, (*e*) 0.75 M and (*f*) 1.0 M

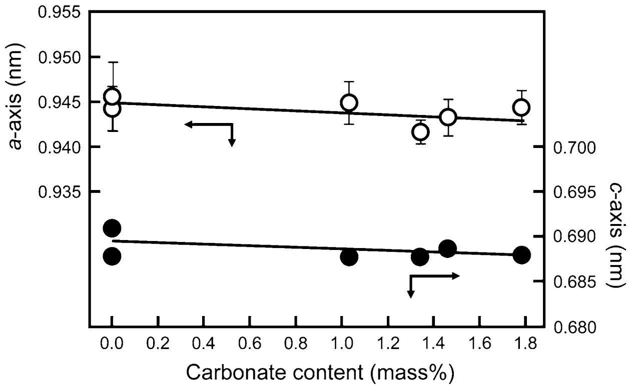


Fig. 7 Lattice parameters (*a*- and *c*-axis) decreased with increase in ammonium carbonate concentration. Standard deviation bars are not shown for *c*-axis as the error was negligible

behavior differs from the previous observations on change of lattice parameters owing to carbonate substitution [16]. The volume of the unit cell slightly decreased with increasing carbonate concentration in the solution.

3.3 Morphology

Figure 8 shows SEM images of the surface of prepared blocks. Needle-like crystal with an average size of 1–2 μm was observed on the control sample. The size of the crystals was smaller than that of the sample reported previously [10]. The size of the crystals was well affected by the pH of the solution used in the hydrothermal processing. The present experiment on preparation of the control sample was carried out with pH of the ammonia buffer raised to 9.12, while Watanabe et al. [10] carried out the preparation at a pH of 7.3. High basicity of the buffer stunted the growth of CDHA particles. On the processing using ammonium carbonate solution, rod-like crystals with an average size of 10–15 μm was observed on 0.01MCHAp (Fig. 8b). The increase in size was significant when compared with the control sample. The 0.01 M ammonium carbonate solution had lower potential of buffering effect and leads to decrease in pH of the solution after exposure of the calcium phosphates. The pH of the solutions were not adjusted to any specific value but had an average value of 9. The CO_3^{2-} incorporation into the lattice of CDHA was low and this relatively permitted free growth of CDHA. Figure 8c shows the morphology on 0.25MCHAp. Small rods of average size 1 μm were arranged in a rosette-shaped morphology. Figures 8d, e and f show that samples 0.5MCHAp, 0.75MCHAp and 1.0MCHAp had irregular-shaped particles owing to increase in the carbonate concentration.

4 Discussion

Hydrothermal processing is a method that produces well-crystallized HAp crystals [17, 18]. The double-step hydrothermal processing give easy formation of calcium phosphate blocks even when the starting material contains highly soluble calcium phosphate such as DCPD. The double-step hydrothermal processing takes advantage of the fact that initial treatment of calcium phosphates with vapors of the solvent requires less solution than immersion in the solution. Vapor treatment prevents rapid reaction of calcium phosphates among themselves and results in better adhesion among the particles in the starting materials. On the vapor treatment of the calcium phosphate mixture, surface of the calcium phosphate block would be converted

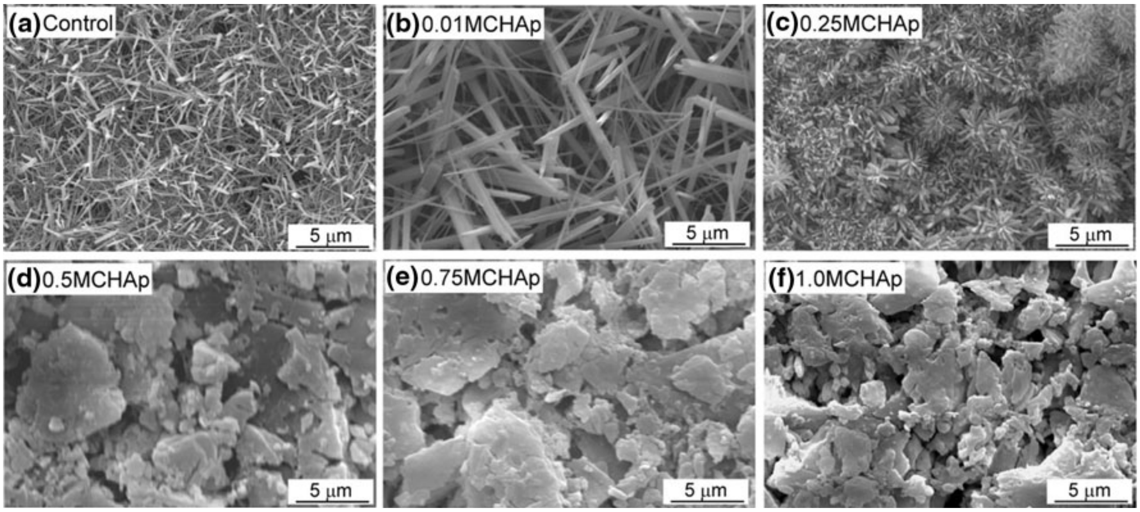


Fig. 8 SEM images on the surface of the samples of **(a)** control and the samples prepared by the double-step hydrothermal processing using an ammonium carbonate solution at initial concentration of **(b)** 0.01 M, **(c)** 0.25 M, **(d)** 0.5 M, **(e)** 0.75 M and **(f)** 1.0 M

to CDHA, thereby making the block hard to withstand solution immersion. The second step is to immerse the calcium phosphate block in the solution to facilitate the homogenous conversion of calcium phosphates to its final product. Complete conversion with growth of the CDHA takes place under the liquid condition that gives enough solvent. Consequently, the vapor treatment lead to nucleation and crystal growth of the CDHA on the surface of the calcium phosphate, while the liquid treatment gave crystal growth of the CDHA as well as complete conversion of the calcium phosphate to CDHA. Thus the double-step hydrothermal processing allows formation of CDHA compacts from highly soluble calcium phosphates.

Addition of ammonium carbonate in the solution for the double-step hydrothermal treatment distinctly affected the formation of CDHA. In the vapor treatment, ammonium carbonate would have decomposed to release carbon dioxide (CO_2), which coexists with water vapor. We speculate that nucleation of CHAp on the surface and adhesion among calcium phosphate particles would be established during the vapor treatment. Following the vapor treatment, the calcium phosphate block was immersed in the ammonium carbonate solution to conduct conversion to CHAp under the existence of carbonate ion. The increase in the initial concentration of ammonium carbonate gave changes in compositions and crystalline morphology of the formed CHAp.

When the ammonium carbonate was not added to the solution, rod-shaped CDHA crystals with an average size of 1–2 μm were formed on the control sample that was treated in the NH_4Cl/NH_3 buffer. In the previous report [10], NH_4Cl/NH_3 buffer adjusted to a pH of 7.3 produced CDHA crystals of approximately 50–60 μm in length. The low pH of the solution gives low degree of supersaturation with respect to the CDHA. So the low degree of supersaturation gives slow growth of CDHA to result in large size of the crystals. From the results of the control sample, Ca/P atomic ratio shows 1.60, which is less than that of stoichiometric composition (Ca/P = 1.67). HAp prepared by wet chemical methods is mostly non-stoichiometric in nature, because stoichiometry of a material depends on the thermodynamic and kinetic factors of the experimental system at equilibrium conditions. Also, the inclusion of carbonate ions in the CDHA system changes the stoichiometry as it substitutes both phosphate and hydroxide ions in CDHA. Another factor might be the presence of acid phosphate ($HPO_4{}^{2-}$), which causes the proportion of OH^- ions to be higher than the stoichiometric value. All these factors contribute to the non-stoichiometry and leads to formation of carbonate substituted CDHA. The chemical composition of the synthesized CDHA, assuming there would be no vacancy in the lattice of CDHA can be given by the formula

$$Ca_{9.60}(HPO_4)_{0.80}(PO_4)_{5.20}(OH)_2.$$

When the CDHA was synthesized under the condition with ammonium carbonate, the Ca/P atomic ratios of the samples increased with increasing concentration of ammonium carbonate in the solution up to 0.75 M at initial concentration, to result in approximately 1.5 mass% of carbonate in the resultant samples. The samples hydrothermally treated with ammonium carbonate decreased in length and differed in morphology with increasing concentration. Sample 0.01MCHAp possessed rod-like crystals with an average length of 10–15 μm. The pH of ammonium carbonate solution showed a remarkable decrease to 6.36 during the first cycle for 12 h, and further decreased to 7.78 after second cycle for 12 h, while the fresh ammonium carbonate solution approximately showed pH = 9. The decrease in pH is attributed to the release of phosphoric acid during hydrolysis of initial reactants of *β*-TCP and DCPD to CDHA. Hydrolysis of *β*-TCP and DCPD to HAp takes place as given by the equations, assuming stoichiometric formulation:

$$10Ca_3(PO_4)_2 + 6H_2O \rightarrow 3Ca_{10}(PO_4)_6(OH)_2 + 2PO_4^{3-} + 6H^+$$

$$10CaHPO_4 \cdot 2H_2O \rightarrow 10CaHPO_4 + 20H_2O$$
$$\rightarrow Ca_{10}(PO_4)_6(OH)_2 + 4PO_4^{3-} + 12H^+ + 18H_2O$$

These reactions lead to decrease in pH of the solution to result in decreased degree of supersaturation with respect to CDHA. Low degree of supersaturation relates slow growth of crystals to result in increase of the crystal size.

From the compositional changes in the prepared samples, increase in Ca/P atomic ratios was observed in the initial concentrations ranging from 0.01 to 0.5 M of ammonium carbonate. The increase in Ca/P atomic ratio is generally attributed to substitution of phosphate ions with carbonate ions (B-type substitution), while the substitution of hydroxide with carbonate (A-type substitution) does not alter the Ca/P atomic ratio. However, FT-IR spectra of the samples indicated both A- and B-type substitution. Thus the existence of ammonium carbonate during the synthesis contributed to substitution of both phosphate and hydroxide sites with carbonate ions, but may mainly contribute to substitution of phosphate site up to 0.75 M of initial concentration. At high initial concentration, 1.0 M of ammonium carbonate gave low Ca/P atomic ratio compatible to that in without ammonium carbonate. This decrease in Ca/P ratio to 1.60 can be attributed to the crystallographic substitution of carbonate ions in the HAp structure. The substitution of carbonate ions for phosphate ions (B-type substitution) results in increase in Ca/P atomic ratio of the samples. The other substitution in which the carbonate substitutes for hydroxide ion (A-type) does not affect the Ca/P atomic ratio of the synthesized material. Since the exact type of substitution is difficult to determine, at this high concentration the substitution would have been more towards A-type than B-type substitution. The broad X-ray diffraction pattern for sample 1.0MCHAp confirms carbonate incorporation in the lattice. The high partial pressure of carbon-dioxide (CO_2) inside the hydrothermal setup would have led to this preferential substitution, thereby unchanging the Ca/P atomic ratio, which is equal to the control sample's value.

When the initial concentration of ammonium carbonate was more than 0.25 M, the ammonium carbonate maintains high pH in the solution. The higher pH gave high degree of supersaturation with respect to CDHA and increased the nuclei numbers. On the other hand, the higher concentration of ammonium carbonate in the initial solution gave irregular-shaped particles with low crystallinity, especially when the initial concentration of ammonium carbonate was 0.5 M and more. The contents of carbonate incorporated in the samples were dependent on the initial concentration of ammonium carbonate in the solution. Moreover, the higher concentration of carbonate ions suppressed the crystal growth of the CDHA with increasing ammonium carbonate to result in smaller crystals, which varied the morphology from rod-shaped to irregular-shaped particles. The X-ray diffraction patterns of the samples with irregular particles also indicated formation of CDHA with low crystallinity due to their broader diffraction peaks than those on the diffraction patterns of the samples with rod-shaped particles. This means that the higher concentration of ammonium carbonate during the synthesis contributed to the formation of CDHA with disordered structure.

Regarding crystal growth, carbonate ions acts as inhibitor of crystal growth to result in low crystallinity and irregular shape. The presence of carbonate ions in the liquid for the hydrothermal processing affects the morphology of the resultant crystals. The substitution of carbonate ions on the B-site of CDHA significantly decreases the length of crystallographic *a*-axis and slightly increases the length of *c*-axis [16]. However, the changes of the lattice parameters in this study are caused both by A- and B-type substitutions. The substitution of carbonate ions on both the sites might have caused a local rearrangement of ions in the CDHA structure. This would have led to decrease in *a*- and *c*-axes of the unit cell with increase in carbonate substitution. From the morphology and diffraction patterns of the CDHA synthesized in the condition where ammonium carbonate existed, well-crystallized AB-type CHAp block containing 1.0 mass% carbonate ions with Ca/P ratio of 1.64 was successfully synthesized through the double-step hydrothermal synthesis.

5 Conclusion

CHAp block was successfully synthesized by employing double-step hydrothermal processing. The morphology of the formed CHAp varied as a function of the initial concentration of ammonium carbonate, to result in needle, rosette- and irregular-shaped crystals. A remarkable inhibition of crystal growth on the samples was observed on the preparation under existence of ammonium carbonate at more than 0.25 mol dm^{-3} in initial concentration. The result establishes that morphology control can be achieved through double-step hydrothermal processing by controlling the experimental parameters.

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